

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 974 614 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

26.01.2000 Bulletin 2000/04

(51) Int. Cl.⁷: C08G 77/455, C08G 69/42

(21) Application number: 99113537.7

(22) Date of filing: 06.07.1999

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 13.07.1998 US 114381

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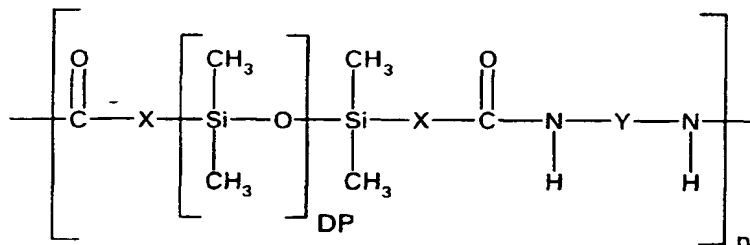
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(54) Method of making siloxane-based polyamides

(57) A method is disclosed for making siloxane-based polyamides which include at least one repeating unit represented by the formula



wherein X is a linear or branched C₁-C₃₀ alkylene chain; Y is a linear or branched C₁-C₂₀ alkylene chain; DP is an integer having a value of 10-500; n is an integer having a value of 1-500. Said method involves heating an intimate reaction mixture containing an olefinic acid and an organic diamine at a temperature greater than 100°C. and forming an organic diamide; and thereafter reacting the organic diamide with a hydride-terminated polydimethylsiloxane in the presence of a hydrosilylation catalyst to form a siloxane-based polyamide.

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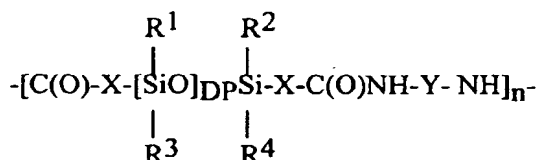
Description

[0001] This invention is directed to a novel method of making siloxane-based polyamides. There is a growing demand in the personal care industry for polymeric materials capable of thickening dimethylcyclsiloxanes to modify product viscosity for various market niches, such as hair, skin, cosmetic and underarm applications. We introduced an effective method in a prior application, United States Serial No. 08/904,709, filed August 1, 1997, and entitled "Cosmetic Composition Containing Siloxane-Based Polyamides as Thickening Agents". However, said application is directed to just one type of a process for preparing siloxane-based polyamides, involves many steps which results in cost prohibitive products that are difficult to implement at commercial scale.

[0002] In our former application, a dimethyl hydride endblocked polydimethylsiloxane is first prepared containing the appropriate number of siloxane units to achieve a desired degree of polymerization (DP). The carboxylate group of undecylenic acid is then protected through reaction with hexamethyldisilazane. The dimethyl hydride endblocked polydimethylsiloxane and the protected undecylenic acid are reacted to produce a siloxane diacid, i.e., a carboxydecyl terminated polydimethylsiloxane. This reaction is accomplished in the presence of a platinum catalyst and the product is washed with methanol to remove the trimethylsilyl protecting group from the protected siloxane diacid. The siloxane diacid is then reacted with an organic diamine to produce a siloxane-based polyamide.

[0003] Accordingly, we have discovered a new process that eliminates many of the otherwise costly steps involved in the process according to our former application.

[0004] Our new process involves the addition of an olefinic acid with an organic diamine to produce an organic diamide. Once the olefinic acid and the organic diamine are fully reacted, an =SiH endblocked polysiloxane is added in the presence of a platinum catalyst, to produce a siloxane-based polyamide via hydrosilylation. The resulting polymeric product is in the form of a high molecular weight thermoplastic polymer. This process is beneficial because it allows for the production of a cost effective manufactured product in commercial quantity. Our invention provides a method of forming siloxane-based polyamides which are useful as thickening agents to formulate a variety of cosmetic compositions. The polyamides of this invention are multiples of a unit represented by the following Formula A:



(1) The degree of polymerization (DP) is 1-700, preferably 10-500, and more preferably 15-45. DP represents an average value for degree of polymerization of the siloxane units in the polymer with greater or lesser DP values centered around the indicated DP value.

(2) n is 1-500, particularly 1-100, and more particularly 4-25.

(3) X is a linear or branched chain alkylene having 1-30 carbons, particularly 3-10 carbons, and more particularly 10 carbons.

(4) Y is a linear or branched chain alkylene having 1-40 carbons, particularly 1-20 carbons, more particularly 2-6 carbons, and especially 6 carbons wherein

(a) The alkylene group may optionally and additionally contain in the alkylene portion at least one of (i) 1-3 amide linkages; (ii) a C5 or C6 cycloalkane; or (iii) phenylene, optionally substituted by 1-3 members which are independently C1-C3 alkyls; and

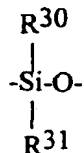
(b) the alkylene group itself may optionally be substituted by at least one of (i) hydroxy; (ii) a C3-C8 cycloalkane; (iii) 1-3 members which are independently C1-C3 alkyls; phenyl, optionally substituted by 1-3 members which are independently C1-C3 alkyls; (iv) a C1-C3 alkyl hydroxy; or (v) a C1-C6 alkyl amine; and

(c) Y can be Z where Z is T(R²⁰)(R²¹)(R²²) where R²⁰, R²¹ and R²² are each independently linear or branched C1-C10 alkyls; and T is CR in which R is hydrogen, the group defined for R¹-R⁴ or a trivalent atom such as N, P and Al.

(5) Each of R¹-R⁴ (collectively "R") is independently methyl, ethyl, propyl, isopropyl, a siloxane chain or phenyl, wherein the phenyl may optionally be substituted by 1-3 members which are methyl or ethyl. More particularly, R¹-R⁴ are methyl or ethyl, especially methyl.

(6) X, Y, DP and R¹-R⁴ may be the same or different for each polyamide unit.

[0005] By "siloxane chain" is meant a group of units such as:



where R³⁰ and R³¹ are each independently organic moieties; and each R³⁰ and R³¹ are connected to silicon by a carbon-silicon bond.

[0006] The carbon numbers in the alkylene chain do not include the carbons in the extra segments or substitutions. Also, the polyamides must have a siloxane portion in the backbone and optionally may have a siloxane portion in a pendant or branched portion.

[0007] If repeated with no variations in the defined variables, Formula A is representative of a linear homopolymer. Variations of the invention include: (1) polyamides in which multiple values of DP and of units X, Y and R¹-R⁴ occur in one polymeric molecule and wherein the sequencing of these units may be alternating, random or block; (2) polyamides in which an organic triamine or higher amine such as tris(2-aminoethyl)amine replaces the organic diamine in part, to produce a branched or crosslinked molecule; and (3) physical blends of any of (1) and (2) and/or linear homopolymers.

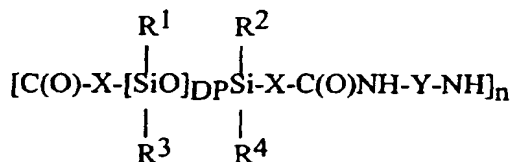
[0008] Our present invention provides a new process for making siloxane-based polyamides. As it relates to our former application, our new process eliminates costly steps and produces a polymer with higher molecular weights than achieved with the previous process in our former application. For example, average molecular weights as measured by gel permeation chromatography (GPC), using the process according to our former application were determined to be approximately 50,000. The new process according to the present invention produces average molecular weights of approximately 65,000.

[0009] In addition, the process according to our instant invention is faster than the particular process of our former application as well as other traditional processes for making siloxane-based polyamides. Our former application process takes approximately four days to make a finished siloxane-based polyamide polymer, while the new route according to the present invention takes approximately one day. The thermoplastic polymer produced as a result of the instant process is ideal for the thickening of dimethylcyclodioxanes, which renders it of benefit in a large number of personal care product applications.

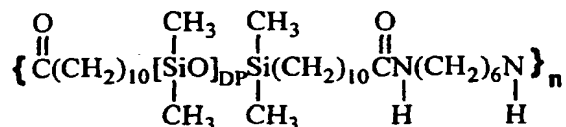
[0010] Our new process involves the addition of an olefinic acid such as undecylenic acid H₂C=CH(CH₂)₈COOH to an organic diamine such as hexamethylene diamine H₂N(CH₂)₆NH₂, to produce an organic diamide. This organic diamide product is then reacted with an =SiH endblocked polysiloxane in the presence of a platinum catalyst to produce the siloxane-based polyamide. Analysis using GPC confirm and indicate the achievement of high molecular weight growth using the process according to the present invention.

[0011] Some examples of compounds of Formula A include:

1) Polyamides of Formula I:

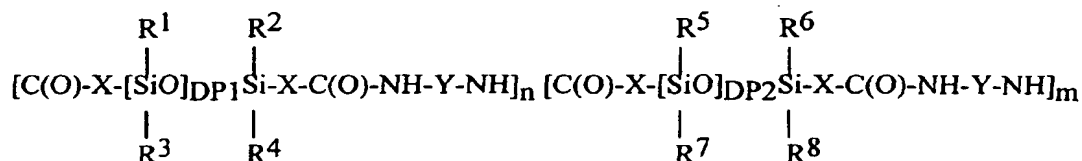


where X, Y, n, R¹-R⁴ and DP are as defined for Formula A. A particular subgroup of Formula I are compounds where R¹ R², R³ and R⁴ are each methyl. Preferred polyamides of Formula I are:



where DP is 10-500, particularly 15-45, and more particularly 29. Another particular group contains polyamides of Formula I where X, Y, DP and R¹-R⁴ are the same in each unit of the polymer.

2) Polyamides containing multiple siloxane block lengths as shown in Formula II:

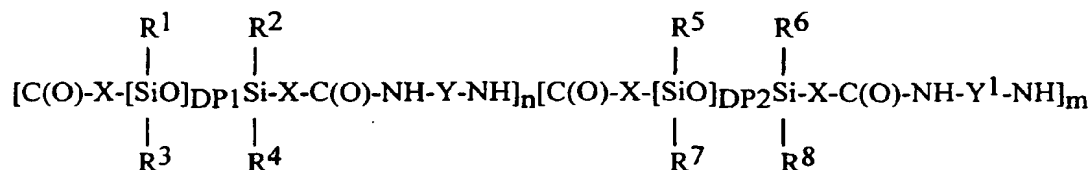


where X, Y, n and R¹-R⁴ have the meanings described above for Formula A; m is the same as the value defined for n; and n and m denote the total number of units enclosed within the brackets; with the individual units arranged with regular, alternating, block or random sequencing.

R⁵-R⁸ is the same group as defined for R¹-R⁴; DP1 and DP2 may be the same or different and each can be independently the same as defined for DP. The units denominated by n and m may be structured to form either block (regularly sequenced) or random copolymers.

A particular subgroup for compounds of Formula II may have methyl for all R groups. Another particular subgroup of compounds of Formula II may have DP1 equal to DP2. A third particular subgroup may have methyl for all R groups and DP1 equal to DP2.

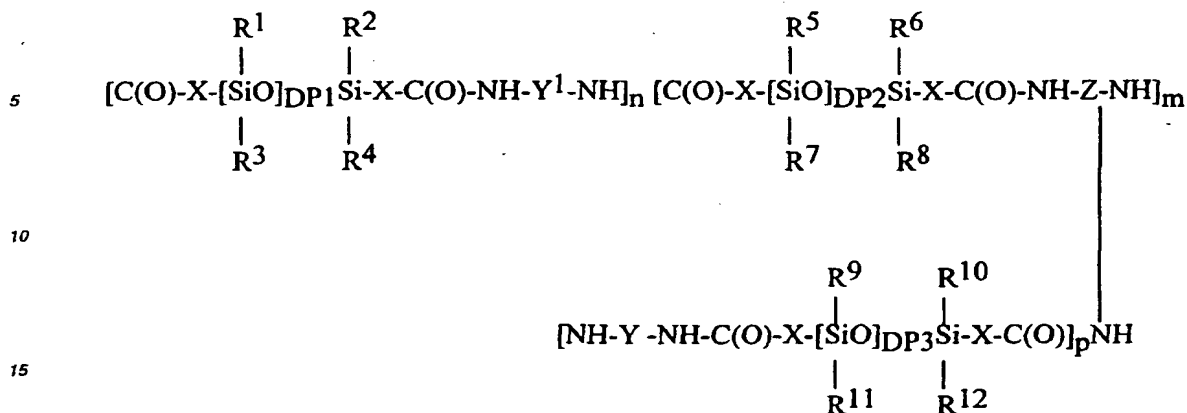
3) Polyamides synthesized from multiple diamines as shown in Formula III:



where X, Y, m, n, R¹-R⁸, DP1, DP2 have the same meanings as described above for Formula A and Formula II; Y¹ is independently selected from the same group as defined for Y; and the units denominated by n and m may be structured to form either block (regularly sequenced) or random copolymers.

A particular subgroup of compounds of Formula III may have DP1 equal to DP2. Another particular subgroup of compounds of Formula III may have methyl for all R groups. A third particular subgroup may have methyl for all R groups and DP1 equal to DP2.

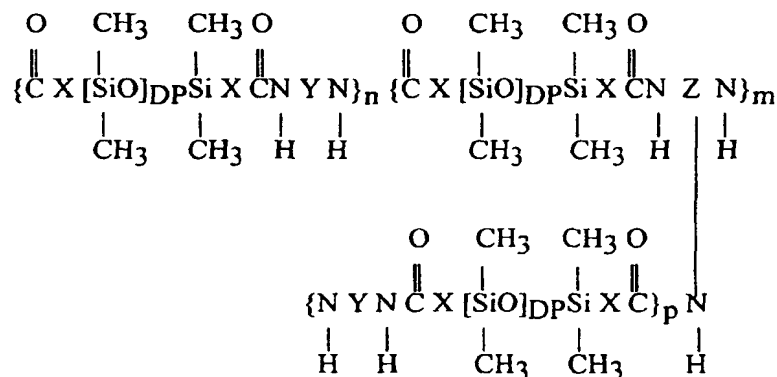
4) Polyamides synthesized with a trifunctional amine as shown in Formula IV:



where X, Y, Y¹, R¹-R⁸, m, n, DP1 and DP2, are the same as defined above; R⁹-R¹² are the same as defined for R¹-R⁸; DP3 is the same as defined for DP; p is the same as defined for m and n; Z is T(R²⁰)(R²¹)(R²²) where R²⁰, R²¹ and R²² are each independently linear or branched C1-C10 alkyls; and T is CR where R is hydrogen, the same as defined for R¹-R⁴ or a trivalent atom such as N, P and Al.

[0012] Preferred values for p are 1-25, with more preferred values being 1-7. Preferred units for R¹-R¹² are methyl. T is preferably N. Particular values for DP1 to DP3 are 10-500, and more particularly 15-45. R²⁰, R²¹ and R²² are preferably ethylene. A preferred group representative of Z is (-CH₂CH₂)₃N.

[0013] One particular group of compounds of Formula IV is represented by the formula



where X is -(CH₂)₁₀-, Y is -(CH₂)₂-; DP is 15-45; m is 5-20% of n + p; and Z is (-CH₂CH₂)₃N.

[0014] Siloxane-based polyamides according to this invention (1) contain both siloxane groups and amide groups which facilitate the thickening of compositions containing volatile silicone fluids and non-volatile silicone fluids; (2) are non-flowable solids at room temperature; and (3) dissolve in a fluid which contains silicone at a temperature of 25-160°C., to form translucent or clear solutions at a temperature in this range.

[0015] With regard to the siloxane units in the siloxane-based polyamides, the siloxane units must be in the main or backbone chain but can also optionally be present in branched or pendent chains. In the main chain, the siloxane units occur in segments as described above. In the branched or pendent chains, the siloxane units can occur individually or in segments.

[0016] Particular groups of siloxane-based polyamides include:

- (a) polyamides of Formula I where the DP is 15-50;
- (b) physical blends of two or more polyamides wherein at least one polyamide has a value for DP in the range of 15-50, and at least one polyamide has a value for DP in the range of 30-500;

(c) compounds of Formula II where (1) the value for DP1 is 15-50 and the value for DP2 is 30-500; and (2) the portion of the polyamide having DP1 is 1-99 weight % based on the weight of the total polyamide content and the portion of the polyamide having DP2 is 1-99 weight %;

(d) physical blends of polyamides of Formula I made by combining (1) 80-99 weight % of a polyamide where n is 2-10, and especially where n is 3-6; and (2) 1-20 weight % of a polyamide where n is 5-500, especially where n is 6-100;

(e) polyamides of Formula III where at least one Y or Y^1 contains at least one hydroxyl substitution;

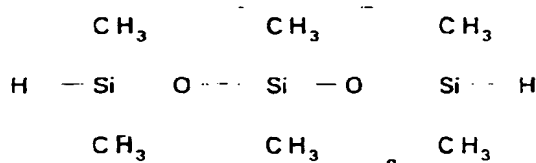
(f) polyamides of Formula A synthesized with at least a portion of an activated diacid, such as a diacid chloride, dianhydride or diester, instead of the diacid;

(g) polyamides of Formula A where X is $-(CH_2)_3-$; and

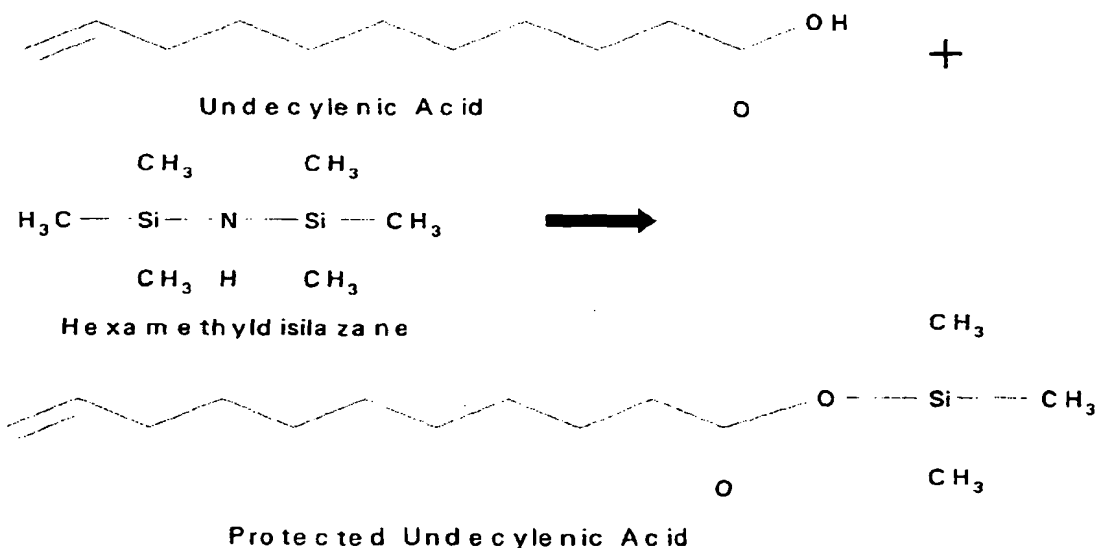
(h) polyamides of Formula A where X is $-(CH_2)_{10}-$.

[0017] A reaction scheme for making polyamides of Formula I according to our former application involves the condensation of a siloxane diacid with an organic diamine as shown below.

(1) A dimethyl hydride endblocked polydimethylsiloxane, such as one of the type shown below, is prepared containing the appropriate number of siloxane units " n " to achieve the desired value of DP.

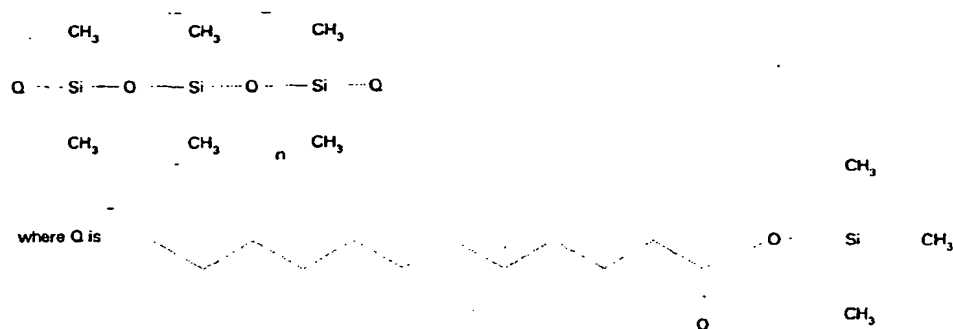


(2) The carboxylic acid group of undecylenic acid is protected through reaction with hexamethyldisilazane $(\text{CH}_3)_3\text{Si-NH-Si}(\text{CH}_3)_3$. This step is shown below.

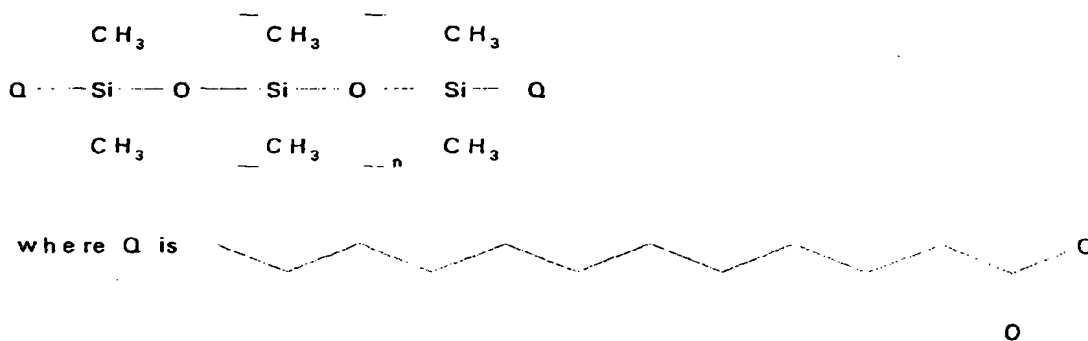


(3) The dimethyl hydride endblocked polydimethylsiloxane and the protected undecylenic acid (the products of Steps (1) and (2)) are reacted to produce a siloxane diacid (carboxydecyl terminated polydimethylsiloxane). This reaction is accomplished in the presence of a platinum catalyst such as chloroplatinic acid and the product is

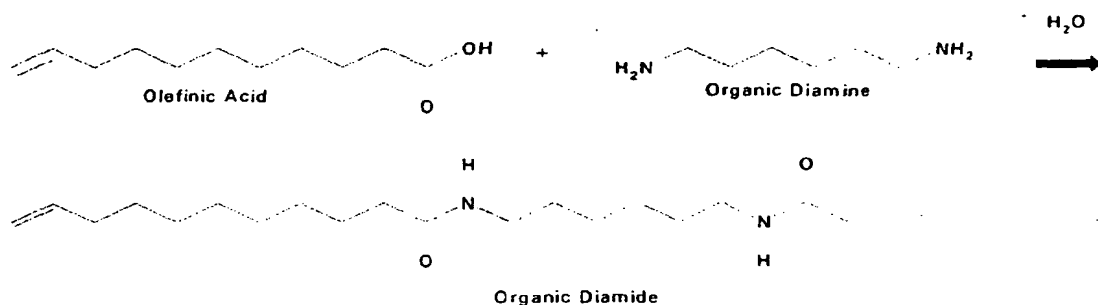
washed with methanol to remove the trimethylsilyl protecting group from the protected siloxane diacid shown below.



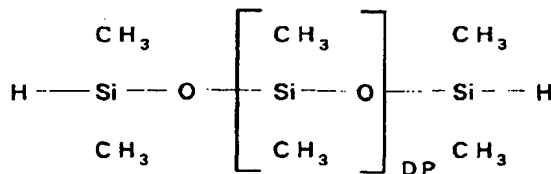
(4) The siloxane diacid (product of Step (3)) is reacted with an organic diamine to produce a siloxane-based polyamide. The siloxane diacid is shown below. This reaction may involve the use of a reaction solvent such as toluene or xylene.



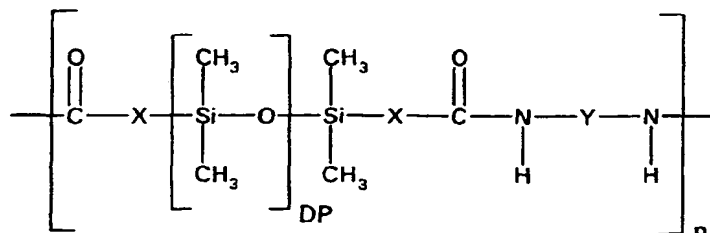
[0018] The simplified process of the present invention can be illustrated schematically with reference to the following reaction scenario in which an olefinic acid is reacted with an organic diamine to produce an organic diamide.



[0019] The organic diamide is then reacted with a hydride-terminated polydimethylsiloxane of the structure such as the one depicted below:



in the presence of a hydrosilylation catalyst to form a siloxane-based polyamide which includes at least one repeating unit represented by the formula

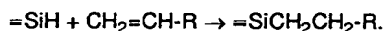


wherein X is a linear or branched C_1 - C_{30} alkylene chain; Y is a linear or branched C_1 - C_{20} alkylene chain; DP is an integer having a value of 10-500; n is an integer having a value of 1-500.

[0020] Suitable olefinic acids which can be used include undecylenic acid $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_8\text{COOH}$, acrylic acid $\text{H}_2\text{C}=\text{CHCOOH}$, 3-butenic acid (vinylacetic acid) $\text{H}_2\text{C}=\text{CHCH}_2\text{COOH}$, 4-pentenoic acid $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{COOH}$ and other olefinic acids with carbon chains of varying length.

[0021] Organic amines which can be used herein preferably include linear alkyl diamines such as hexamethylene diamine, ethylene diamine and mixtures of linear alkyl diamines, as well as other amines such as decamethylene diamine.

[0022] A platinum catalyzed hydrosilylation reaction is employed according to this invention. Generally, hydrosilylation involves the reaction between a polysiloxane containing $=\text{Si-H}$ groups and a material containing unsaturation, e.g., vinyl groups. Some attractive features of this mechanism are that no by-products are formed and hydrosilylation will proceed even at room temperature. In the mechanism, crosslinking involves addition of $=\text{SiH}$ across double bonds, i.e.,



[0023] The process requires a catalyst to effect the reaction between the $=\text{SiH}$ containing polysiloxane and the material containing unsaturation, i.e., the organic diamide in the case of the present invention. Suitable catalysts are Group VIII transition metals, i.e., the noble metals. Such noble metal catalysts are described in US Patent 3,923,705 which show platinum catalysts. One preferred platinum catalyst is Karstedt's catalyst, which is described in Karstedt's US Patents 3,715,334 and 3,814,730. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex typically containing one weight percent of platinum in a solvent such as toluene. Another preferred platinum catalyst is a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation. It is described in US Patent 3,419,593. Most preferred as the catalyst is a neutralized complex of platinumous chloride and divinyl tetramethyl disiloxane, for example, as described in US Patent 5,175,325.

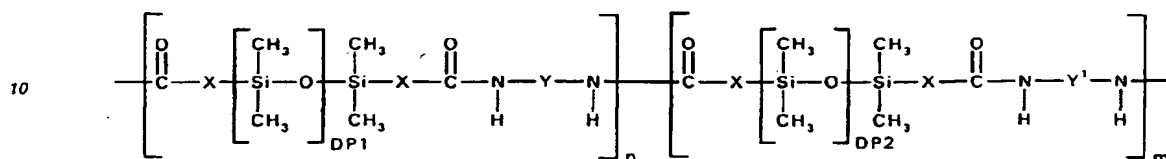
[0024] The noble metal catalyst can be used in an amount of from 0.00001-0.5 parts per 100 weight parts of the $=\text{SiH}$ containing polysiloxane. Preferably, the catalyst should be used in an amount sufficient to provide 5-15 parts per million (ppm) Pt metal per total composition.

[0025] Carrying out of the process is simply a matter of combining the $=\text{SiH}$ containing polysiloxane(s), the material containing unsaturation, i.e., the organic diamide and the catalyst; and mixing these ingredients. The reaction temperature can vary over a wide range and the optimum temperature is dependent upon the concentration of the catalyst and the nature of the reactants. Ordinarily, it is best to keep the reaction temperature below 300°C . Best results with most reactants are obtained by initiating the reaction at 80°C . to 180°C . and maintaining the reaction within reasonable limits of this range.

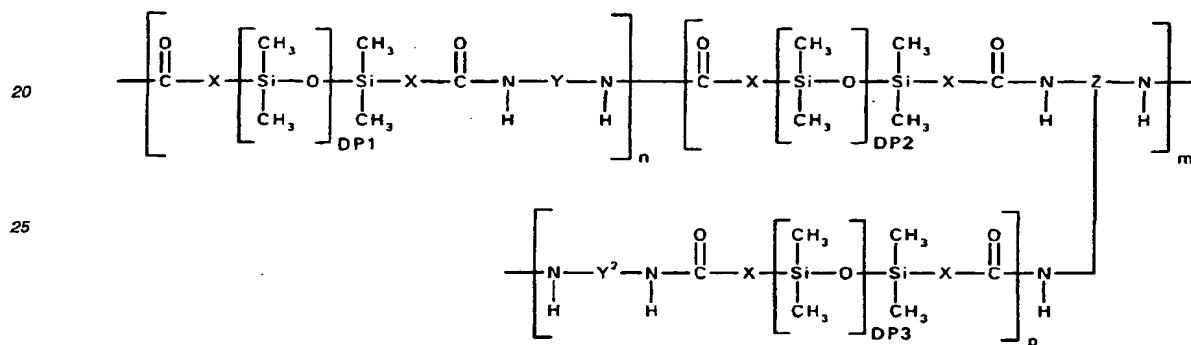
[0026] Typically, our process is carried out using a 1:1 molar ratio of $=\text{Si-H}$ containing polysiloxane and the material

containing unsaturation. It is expected that useful materials may also be prepared by carrying out the process with an excess of either the =Si-H containing polysiloxane or the material containing unsaturation, but this would be considered a less efficient use of the materials.

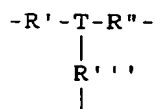
[0027] The process can also be used to make other types of siloxane-based polyamides in which the repeating unit of the siloxane-based polyamide is represented by the formula



or by the formula



wherein X is a linear or branched C₁-C₃₀ alkylene chain; Y, Y¹ and Y² are linear or branched C₁-C₂₀ alkylene chains; DP1, DP2 and DP3 are integers each having values of 10-500; n, m and p are integers each having values of 1-500; Z is represented by



wherein R', R'' and R''' are linear or branched C₁-C₁₀ alkylene groups; and T is CR in which R is hydrogen, methyl, ethyl, propyl, isopropyl, a siloxane chain or phenyl, wherein the phenyl may optionally be substituted by 1-3 members which are methyl or ethyl or T is a trivalent atom such as N, P and Al; provided n is not the same as m, Y is not the same as Y¹ or DP1 is not the same as DP2.

[0028] Following are specific synthesis examples for forming siloxane-based polyamides according to the method of this invention. Unless otherwise indicated, the vacuums described in Examples 1-4 are in the range of 5-20 millimeters of mercury. While particular siloxane-based polyamides are disclosed or used in the following examples, it is to be understood that other siloxane-based polyamides, for example, those made with a purified siloxane diacid, dianhydride, diester or diacid chloride may also be used.

Example 1 - 30 DP Polymer

[0029] A 500 ml three neck flask equipped with a thermometer, electrical stirrer, nitrogen sweep and a condenser was charged with 50.12 g of undecylenic acid and 22.58 g of a 70% hexamethylene diamine mixture in water. The flask was immediately heated to 225°C. and kept at this temperature for 2 hours. After 2 hours, a vacuum was applied to the system for 2 hours to remove any unreacted materials. Upon completion of vacuum stripping, the flask was reweighed to obtain the product weight. The temperature was increased to 120°C. and 65 g of toluene and 0.5 g of a solution con-

taining platinum in the form of a complex of platinous chloride and divinyl tetramethyl disiloxane, were added to the flask. The temperature was increased to 185°C. and 279.2 g of a 30 DP dimethylhydrogen endblocked polydimethylsiloxane was added to the flask over a 30 minute period. After complete addition, a Dean Stark trap was used to replace the addition funnel on the flask and the toluene was removed from the flask. After removal of the toluene, the materials were allowed to react for an additional period of one hour. Vacuum stripping was applied to the flask for 1 hour to ensure complete removal of any residual solvent. The temperature of the final siloxane-based polyamide was cooled to 150°C. and poured off while still in the melt form.

Example 2 - 20 DP Polymer

[0030] A 500 ml three neck flask equipped with a thermometer, electrical stirrer, nitrogen sweep and a condenser was charged with 55.0 g of undecylenic acid and 24.77 g of a 70% hexamethylene diamine mixture in water. The flask was immediately heated to 225°C. and kept at this temperature for 2 hours. After 2 hours, a vacuum was applied to the system for 2 hour to remove any unreacted materials. Upon completion of vacuum stripping, the flask was reweighed to obtain the product weight. The temperature controller was increased to 120°C. and 65 g of toluene and 0.5 g of a solution containing platinum in the form of a complex of platinous chloride and divinyl tetramethyl disiloxane, were added to the flask. The temperature was then increased to 185°C. and 222.0 g of a 20 DP dimethylhydrogen endblocked polydimethylsiloxane was added to the flask over a 30 minute period. After complete addition, a Dean Stark trap was used to replace the addition funnel on the flask and the toluene was removed from the flask. After removal of the toluene, the materials were allowed to react for an additional period of one hour. Vacuum stripping was applied to the flask for 1 hour to ensure complete removal of any residual solvent. The temperature of the final siloxane-based polyamide was cooled to 150°C. and poured off while still in the melt form.

Example 3 - 15 DP Polymer

[0031] A 500 ml three neck flask equipped with a thermometer, electrical stirrer, nitrogen sweep and a condenser was charged with 57.75 g of undecylenic acid and 24.77 g of a 70% hexamethylene diamine mixture in water. The flask was immediately heated to 225°C. and kept at this temperature for 2 hours. After 2 hours, a vacuum was applied to the system for 2 hours to remove any unreacted materials. Upon completion of vacuum stripping, the flask was reweighed to obtain the product weight. The temperature was increased to 120°C. and 65 g of toluene and 0.5 g of a solution containing platinum in the form of a complex of platinous chloride and divinyl tetramethyl disiloxane were added to the flask. The temperature was then increased to 185°C. and 168.72 g of a 15 DP dimethylhydrogen endblocked polydimethylsiloxane was added to the flask over a 30 minute period. After complete addition, a Dean Stark trap was used to replace the addition funnel on the flask and the toluene was removed from the flask. After removal of the toluene, the materials were allowed to react for an additional period of one hour. Vacuum stripping was applied to the flask for 1 hour to ensure complete removal of any residual solvent. The temperature of the final siloxane-based polyamide was cooled to 150°C. and poured off while still in the melt form.

Example 4 - 10 DP Polymer

[0032] A 500 ml three neck flask equipped with a thermometer, electrical stirrer, nitrogen sweep and a condenser was charged with 67.0 g of undecylenic acid and 29.82 g of a 70% hexamethylene diamine mixture in water. The flask was immediately heated to 225°C. and kept at this temperature for 2 hours. After 2 hours, a vacuum was applied to the system for 2 hours to remove any unreacted materials. Upon completion of vacuum stripping, the flask was reweighed to obtain the product weight. The temperature was increased to 120°C. and 65 g of toluene and 0.5 g of a solution containing platinum in the form of a complex of platinous chloride and divinyl tetramethyl disiloxane were added to the flask. The temperature was then increased to 185°C. and 150.97 g of a 10 DP dimethylhydrogen endblocked polydimethylsiloxane was added to the flask over a 30 minute period. After complete addition, a Dean Stark trap was used to replace the addition funnel on the flask and the toluene was removed from the flask. After removal of the toluene, the materials were allowed to react for an additional period of one hour. Vacuum stripping was applied to the flask for 1 hour to ensure complete removal of any residual solvent. The temperature of the final siloxane-based polyamide was cooled to 150°C. and poured off while still in the melt form.

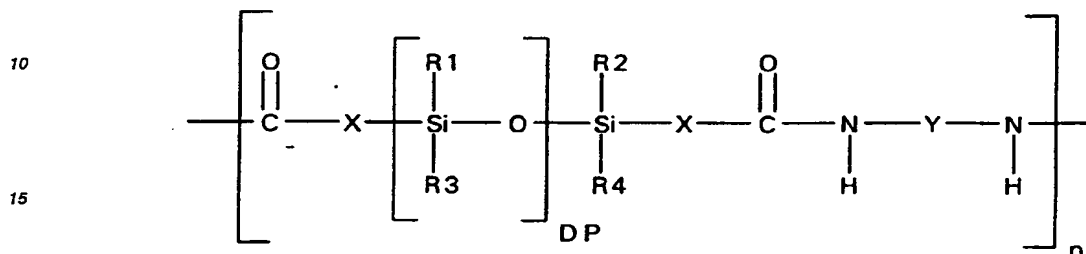
[0033] Although undecylenic acid, acrylic acid, 3-butenic acid (vinylacetic acid) and 4-pentenic acid, have been set forth as being representative examples of some suitable olefinic acids, other branched or straight-chain alkenic acids $C_nH_{(2n-2)}O_2$ can be employed in accordance with the method of the present invention.

[0034] The siloxane-based polyamides according to our present invention can be used as thickening agents in hair, skin, underarm and cosmetic product applications. The siloxane units provide compatibility with silicone fluids such as cyclomethicones, while the amide linkages and the spacing and selection of the locations of the amide linkages, facili-

tate thickening and formation of such products.

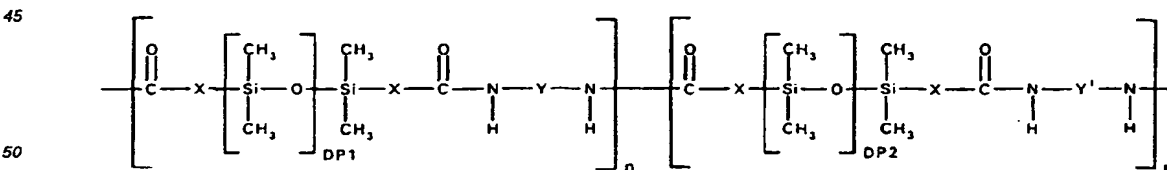
Claims

1. A method of making a siloxane-based polyamide which includes at least one repeating unit represented by the formula

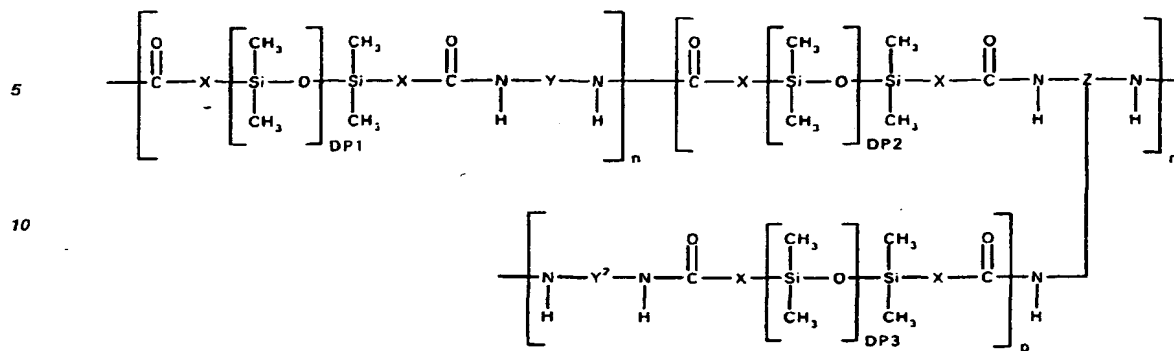


wherein X is a linear or branched C₁-C₃₀ alkylene chain; Y is a linear or branched C₁-C₂₀ alkylene chain; R¹-R⁴ are independently methyl, ethyl, propyl, isopropyl, a siloxane chain, phenyl or phenyl substituted by 1-3 members which are methyl or ethyl; DP is an integer having a value of 10-500; and n is an integer having a value of 1-500; the method comprising heating a reaction mixture containing an olefinic acid and an organic diamine at a temperature greater than 100°C. and forming an organic diamide; and thereafter reacting the organic diamide with a hydride-terminated polydimethylsiloxane in the presence of a hydrosilylation catalyst to form the siloxane-based polyamide.

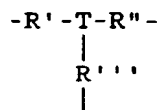
2. A method according to claims 1 in which the organic diamine is a compound having the formula H₂N-R⁵-NH₂ in which R⁵ is an alkylene chain having 1-40 carbon atoms or an alkylene chain having 1-40 carbon atoms which is substituted with C₁-C₄ alkyl groups, phenyl, hydroxyl, carboxyl or amino groups.
3. A method according to claim 2 in which the organic diamine is a compound selected from the group consisting of hexamethylene diamine, ethylene diamine and decamethylene diamine.
4. A method according to claim 1 in which the olefinic acid is a compound selected from the group consisting of undecylenic acid, acrylic acid, 3-butenic acid and 4-pentenoic acid.
5. A method according to claim 1 in which the siloxane-based polyamide has a number average molecular weight of from 4,000 to 200,000 daltons, as determined by gel permeation chromatography using polydimethylsiloxane as a standard.
6. A method according to claim 1 in which the repeating unit of the siloxane-based polyamide is represented by the formula



or the formula



wherein X is a linear or branched C₁-C₃₀ alkylene chain; Y, Y¹ and Y² are linear or branched C₁-C₂₀ alkylene chains; DP1, DP2 and DP3 are integers each having values of 10-500; n, m and p are integers each having values of 1-500; Z is represented by



wherein R', R'' and R''' are linear or branched C₁-C₁₀ alkylene groups; and T is CR in which R is hydrogen, methyl, ethyl, propyl, isopropyl, a siloxane chain or phenyl, wherein the phenyl may optionally be substituted by 1-3 members which are methyl or ethyl, T is a trivalent atom such as N, P and Al; provided n is not the same as m, Y is not the same as Y¹ DP1 is not the same as DP2.